Organic compounds present in the natural Amazonian aerosol: Characterization by gas chromatography–mass spectrometry

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[1] As part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA)-Cooperative LBA Airborne Regional Experiment (CLAIRE) 2001 campaign in July 2001, separate day and nighttime aerosol samples were collected at a ground-based site in Amazonia, Brazil, in order to examine the composition and temporal variability of the natural "background" aerosol. We used a high-volume sampler to separate the aerosol into fine (aerodynamic diameter, AD < 2.5 μm) and coarse (AD > 2.5 μm) size fractions and quantified a range of organic compounds in methanolic extracts of the samples by a gas chromatographic-mass spectrometric technique. The carbon fraction of the compounds could account for an average of 7% of the organic carbon (OC) in both the fine and coarse aerosol fractions. We observed the highest concentrations of sugars, sugar alcohols, and fatty acids in the coarse aerosol samples, which suggests that these compounds are associated with primary biological aerosol particles (PBAP) observed in the forest atmosphere. Of these, trehalose, mannitol, arabitol, and the fatty acids were found to be more prevalent at night, coinciding with a nocturnal increase in PBAP in the 2–10 μm size range (predominantly yeasts and other small fungal spores). In contrast, glucose, fructose, and sucrose showed persistently higher daytime concentrations, coinciding with a daytime increase in large fungal spores, fern spores, pollen grains, and, to a lesser extent, plant fragments (generally >20 μm in diameter), probably driven by lowered relative humidity and enhanced wind speeds/convective activity during the day. For the fine aerosol samples a series of dicarboxylic and hydroxyacids were detected with persistently higher daytime concentrations, suggesting that photochemical production of a secondary organic aerosol from biogenic volatile organic compounds may have made a significant contribution to the fine aerosol. Anhydrosugars (levoglucosan, mannosan, galactosan), which are specific tracers for biomass burning, were detected only at low levels in the fine aerosol samples. On the basis of the levoglucosan-to-OC emission ratio measured for biomass burning aerosol, we estimate that an average of ~16% of the OC in the fine aerosol was due to biomass burning during CLAIRE 2001, indicating that the major fraction was associated with biogenic particles. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; *KEYWORDS:* gas chromatography–mass spectrometry, organic aerosol, Amazon, biogenic aerosol, sugars, sugar alcohols

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1. Introduction

[2] In recognition of its global importance as a naturally functioning system, as well as the magnitude of the land use changes occurring within its bounds, a number of major international scientific field experiments have been carried out in the Amazon Basin over the last two decades, many of them including a strong aerosol research component. Experiments performed during the dry season have focused predominantly on examining the composition, properties and climatic effects of smoke aerosol [*Talbot et al.*, 1988; *Kaufmann et al.*, 1998; *Artaxo et al.*, 2002; *Andreae et al.*,

2002], since these submicrometer particles may efficiently scatter and absorb sunlight, and alter the microphysical structure of clouds, resulting in potential changes to the radiation budget and hydrological cycle. On the other hand, experiments carried out in the wet season, when burning is suppressed by high rainfall frequency, have sought to improve our understanding of the key ''natural'' biological processes occurring within the Amazon rainforest, such as the emission of biogenic aerosol particles [*Artaxo and Maenhaut*, 1990; *Artaxo et al.*, 1990; *Talbot et al.*, 1990; *Artaxo and Hansson*, 1995; *Artaxo et al.*, 2002; *Andreae et al.*, 2002]. The latter studies are especially important for gauging the effects of tropical biomass-burning emissions on the regional and global atmosphere, because they provide a ''background reference'' against which the dry season data can be compared. Even more importantly, they provide information about the natural, biogenically regulated CCN population [*Roberts et al.*, 2001a].

[3] In terms of chemical composition measurements, most work to date on Amazonian aerosols has focused on the determination of elemental concentrations using particle-induced X-ray emission (PIXE) and instrumental neutron activation analysis (INAA), water-soluble ions by ion chromatography (IC), and so-called ''black carbon'' by light attenuation techniques [e.g., *Artaxo et al.*, 1988; *Artaxo and Maenhaut*, 1990; *Talbot et al.*, 1990; *Echalar et al.*, 1998; *Guyon et al.*, 2003a]. This has provided valuable information about aerosol sources and seasonal variations in aerosol composition, since certain elements/ions (or profiles of them) tend to be fairly specific for different sources. Limited studies have shown, however, that organic matter may account for up to 90% of the total aerosol mass in this region [*Formenti et al.*, 2001; *Guyon et al.*, 2003a, 2003b]. Therefore it is important that the analysis of Amazonian aerosols be extended to include detailed characterization of the organic fraction, especially in light of the increasing evidence that organic species may significantly modulate the ability of aerosols to act as cloud condensation nuclei (CCN), the ''seeds'' on which cloud droplets form [*Saxena et al.*, 1995; *Nenes et al.*, 2002].

[4] There have already been some efforts to address this deficiency in our understanding. *Kubátová et al.* [2000] and *Zdráhal et al.* [2001] reported the identification of a number of novel dicarboxylic and tricarboxylic acids in Amazonian aerosols, which may derive from biomass burning or the photo-oxidation of monoterpene compounds emitted by the forest vegetation. *Graham et al.* [2002] and *Zdráhal et al.* [2002] carried out detailed organic speciation studies on a series of samples collected during the 1999 dry season, while *Mayol-Bracero et al.* [2002] provided a more general apportionment of the dry season aerosol, focusing in particular on the water-soluble organic fraction. A major finding of the latter study was that the soluble organic fraction appeared to contain a significant amount of high molecular weight compounds (so-called ''humic-like substances''), rather than being composed solely of simple low-molecular-weight species.

[5] In July 2001, the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA)-Cooperative LBA Airborne Regional Experiment (CLAIRE) 2001 campaign was carried out near Balbina, a small town located in central Amazonia. Although the experiment took place toward the beginning of the dry season, the effects of biomass burning are generally not as pronounced in this area compared to other parts of Amazonia (P. Artaxo, unpublished data, 2002), and there was relatively little influence of anthropogenic emissions on the atmospheric composition. Aspects of the composition and temporal variability of the sampled aerosol are detailed in a companion paper [*Graham et al.*, 2003]. Here, we report on our efforts to characterize part of the organic component of the aerosol. A gas chromatographic-mass spectrometric (GC-MS) technique was employed to identify and quantify a range of organic compounds within the samples, including series of sugars, sugar alcohols, anhydrosugars, short-chain carboxylic acids and long-chain fatty acids.

[6] One of the major features of our study was the adoption of a day-night sampling regime, in order to examine diurnal variations in the concentration and composition of the aerosol. The impetus for this was twofold. Firstly, we wished to further investigate an interesting phenomenon that had been reported of enhanced nighttime concentrations of ''coarse'' aerosol and biogenic-associated elements within tropical forested areas [*Artaxo and Maenhaut*, 1990; *Roberts et al.*, 2001b; *Artaxo et al.*, 2002; *Guyon et al.*, 2003a]. Secondly, since the Amazon Basin is known to emit large quantities of reactive volatile organic compounds (VOCs) (e.g., isoprene and monoterpenes) [*Kesselmeier et al.*, 2000] and the production of hydroxyl radicals is at a maximum in the tropics, the formation of secondary organic aerosol (SOA) via photooxidation processes might be expected to contribute significantly to the natural background aerosol [*Andreae and Crutzen*, 1997; *Kavouras et al.*, 1999a, 1999b]. We were interested to determine whether any highly oxidized organic compounds exhibited higher concentrations during the day, which might be taken as evidence for a likely photochemical source.

2. Sampling and Analytical Methods

2.1. Site Description

[7] Ground-based measurements were performed as part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA)-Cooperative LBA Airborne Regional Experiment (CLAIRE) 2001 in July 2001 at Balbina, Amazonia (1°55′S, 59°24′W, 174 m above sea level). This site is located approximately 100 km north of Manaus, on the southern periphery of the Balbina hydroelectric reservoir, and faces more than 1000 km of pristine rainforest to the east.

2.2. Aerosol Sampling and Analysis

[8] A dichotomous high-volume (HiVol) sampler (~4 m above ground level) was used to collect samples in two size fractions (particles smaller and larger than ~2.5 μm aerodynamic diameter, AD) [*Solomon et al.*, 1983] on Pall Gelman quartz fiber filters (prebaked for 15 hours at 550°C), as described by *Graham et al.* [2002]. While the sampler did not have a well-defined upper cut off, fine wire mesh was placed over the inlet to prevent the entry of insects. Loaded filters were stored in the dark in clean glass jars in a freezer at −18°C until the time of analysis. Separate daytime and nighttime samples were collected. To ensure that we obtained sufficient loadings of aerosol particles for

analysis, aerosol was sampled for three consecutive days or nights using each filter set. Filters were changed at ~0800 and 1800 LT. Between samplings, the filters (still housed in their holders) were wrapped in clean aluminum foil, placed in sealed vessels, and stored in the freezer. A total of three daytime and three nighttime quartz filter sets were collected between 19 July and 28 July.

[9] A series of individual organic compounds within the HiVol quartz filter samples were quantified using a gas chromatographic-mass spectrometric (GC-MS) technique that incorporated a derivatization step designed to convert carboxyl (COOH) and hydroxyl (OH) functional groups to trimethylsilyl esters and ethers, respectively. The method used was adapted from one described previously for the quantitation of water-soluble organic compounds in aerosol samples from the dry season [*Graham et al.*, 2002]. In order to obtain sufficient material for analysis, much larger filter portions had to be extracted in the current study because of the substantially lower aerosol loadings compared to the dry season. This in turn necessitated the use of larger amounts of solvent for the extraction step. Water proved to be unsuitable for this purpose because of the significant and irreproducible losses of analytes that occurred upon evaporation prior to derivatization. Methanol was thus chosen as a substitute because of its high polarity and relatively low boiling point.

[10] For each sample, a minimum of 12 punches (1.5 cm diameter) were placed in a silylated 250 mL round-bottomed flask. 50 mL of methanol was then added, together with 100 μL of an aqueous internal standard mixture containing 3, 3-dimethylglutaric acid, phenyl-ß-D-glucoside, and 4-hydroxybutyric acid. The mixture was shaken for 20 s every 5 min with a vortex agitator over a period of 30 min, and then filtered through a clean glass sinter. The filter fibers were extracted twice more with two 50 mL methanol aliquots in the same fashion. The combined filtrates were then concentrated to ~1 mL at 35°C using a rotary evaporator, then transferred to a 3 mL borosilicate glass vial and blown to dryness with a gentle stream of pure nitrogen. The dried residue was derivatized by adding 75 μL of bis(trimethylsilyl)trifluoroacetamide (BSTFA) (containing 1% trimethylchlorosilane (TMCS) as a catalyst) and 75 μL pyridine, capping the vial, and heating at 70°C for 15 min. After cooling to room temperature, samples were analyzed within 2 hours using a Hewlett-Packard (HP) 6890 GC-MS fitted with a HP-5MS capillary column (5% phenyl-methylsiloxane, 30 m × 0.25 mm I.D., 0.25 μm thick film) and Supelco guard column (deactivated methylsiloxane, 5 m × 0.32 mm I.D.). The operating conditions were: injection port temperature, 280°C; interface temperature, 280°C; column oven temperature, 65°C for 10 min, ramped at 10°C min^{-1} to 310°C with a 15 min hold; helium carrier gas (flow rate of 1.4 mL min^{-1} at 75°C); 1 μL injection volume; electron impact ionization at 70 eV. The split/splitless injector was operated in the splitless mode for 1 min after injection of the sample. The mass spectrometer was operated in the full scan mode in the *m*/*z* range of 50 to 500. Identification of compounds was achieved using the 6th edition of the Wiley mass spectral database, and then by comparing the mass spectra and retention times of the chromatographic peaks with those of authentic samples obtained from Sigma Chemical Co. For quantitation, calibration curves were constructed by analyzing aliquots of a stock solution of authentic standards that had been evaporated and derivatized in the fashion described above. Quantitation was performed on extracted ion chromatograms. Duplicate analyses showed that the precision of the determination is typically 20%; however, a number of odd-carbon fatty acids in both size fractions, and dicarboxylic acids in the coarse aerosol fraction, were frequently close to the detection limit when accounting for the uncertainty of the blank. All reported concentrations are corrected for procedural blanks.

3. Results and Discussion

3.1. Meteorological Conditions

[11] A detailed description of the meteorological conditions encountered during the CLAIRE 2001 campaign is provided by *Graham et al.* [2003], therefore only a brief overview is presented here. For the period of the campaign over which the present set of aerosol samples was collected, airflow over northern Brazil was dominated by synoptic-scale meteorology, with easterly trade winds transporting humid oceanic air masses from the Atlantic Ocean over the forests of the Amazon Basin. Thus the air arriving at Balbina had traveled over approximately a thousand kilometers of remote forest before being sampled. The presence of a large hydroelectric dam to the north of Balbina was found to produce a gentle, yet measurable, lake-land breeze at the sampling site. Strong solar heating of the ground and overlying air, however, produced a deep, convectively well-mixed boundary layer during the day, so that much of the aerosol sampled during the campaign is believed to have still been representative of that present over the forested regions the Amazon Basin. At dusk, radiative cooling was found to result in the formation of a shallow, decoupled nocturnal boundary layer, as has been observed previously in the Amazon Basin [*Garstang et al.*, 1988]. This consistent meteorological pattern was found to produce a distinct diurnal cycle in the composition of the aerosol, as detailed in the sections below.

3.2. General Composition and Diurnal Variability of the Aerosol

[12] Aspects of the composition and temporal variability of the aerosol are discussed in a companion paper [*Graham et al.*, 2003]. In particular, the mass concentration of aerosol with AD between 2 and 10 μm was found to be roughly double that of the aerosol with <2 μm AD, and was found to be consistently higher at night (mean night-to-day ratio = 1.9). This increase was accompanied by elevated nighttime concentrations of elements/ions commonly associated with biogenic matter (P, S, K, Zn, Cu, NH_4^+) in the 2–10 μm AD aerosol fraction, and is therefore believed to reflect the trapping of the forest aerosol under the shallow nocturnal boundary layer [*Roberts et al.*, 2001b], possibly coupled with an active release of certain types of biogenic particles, especially yeasts and other small fungal spores, at night [*Graham et al.*, 2003].

[13] Light microscopy and environmental scanning electron microscopy (ESEM) of samples collected on glass slides, described in detail by *Graham et al.* [2003] and P. E. Taylor et al. (manuscript in preparation, 2003),

confirmed the dominant contribution of primary biological aerosol particles (PBAP) to the aerosol fraction with >2 μm AD, and revealed that the nocturnal increase in aerosol with AD between 2 and 10 μm was due to PBAP. Moreover, these analyses revealed that not only the total concentration, but also the make up of the PBAP, varied between day and nighttime. Specifically, high concentrations of yeasts (2–10 μm in diameter) were found at night (~17 times higher than during the day). The concentrations of "giant" PBAP, however, increased during the day. These included epiphytic *Polypodium* fern spores (20–40 μm diameter), pollen grains (7–26 μm diameter), fern spores (15–50 μm) and some algae (~8 μm). Occasionally, fern sporangia and leaf hairs were also found in the daytime samples, although the latter were quite rare. The higher daytime concentrations of these larger particles was likely due to lowered relative humidity during the day, resulting in the catapulting of fern spores into the air [*Gregory*, 1973], and the opening of pollen-laden flower anthers [*Taylor et al.*, 2002], coupled with stronger daytime winds and convective activity, causing enhanced entrainment and dispersal of the particles [*Wickmen*, 1994]. Given the limited dispersal range of giant PBAP, it is expected that the species in and immediately surrounding the measurement site, including colonizer species, contributed significantly to the composition of this subset of the aerosol [*Bush and Rivera*, 1998; P. E. Taylor et al., manuscript in preparation, 2003]. Insect activity also appeared to be more intense during the day, with whole or fragmented insects observed in a number of the samples.

[14] Consistent with the dominant contribution of PBAP to the CLAIRE 2001 aerosol, organic carbon (OC) measurements performed on the HiVol filters [*Graham et al.*, 2003] indicated that organic matter accounted for an estimated 80% of the coarse aerosol mass. The OC content of the fine size fraction was found to be almost as large (~70%). ESEM analysis of fine aerosol samples collected on graphite foils (B. Graham et al., manuscript in preparation, 2003) indicated that this was due to the fact that PBAP also accounted for a large fraction of the particles <2 μm AD. SOA, formed via the gas-to-particle conversion of biogenic gases from the rainforest, would also be expected to have made a sizeable contribution to the fine OC concentration [*Went*, 1960; *Andreae and Crutzen*, 1997; *Kavouras et al.*, 1999a, 1999b].

3.3. Organic Speciation of the Fine and Coarse Aerosol

[15] Using our GC-MS technique, we were able to identify and quantify a range of sugars, sugar alcohols, anhydrosugars, short-chain carboxylic acids, and long-chain fatty acids in the samples. Some fatty alcohols, octacosanol in particular, were also detected in the samples, but not quantified. Table 1 provides a summary of the concentration data for both the fine and coarse aerosol fractions, while Figure 1 presents pie diagrams showing the average relative contribution of the different compound classes to the total fine and coarse aerosol mass identified by the GC-MS method, with data segregated into day and nighttime sampling periods. Oxalic acid was detected by the method, but could not be reliably quantified due to the instability of its TMS derivative (possibly due to a high degree of steric interaction between the two TMS groups). Therefore oxalate concentration data derived from the IC analysis of stacked filter unit (SFU) samples collected between 19 July and July 28 [*Graham et al.*, 2003] has been incorporated into Table 1 and Figure 1. It should be noted, however, that the SFU sampler had a well-defined upper cut off of 10 μm, whereas the HiVol sampler did not, so that the concentrations of oxalic acid in the coarse HiVol samples may have been slightly higher.

[16] A discussion of the four different compound classes identified by GC-MS and their probable sources follows.

3.3.1. Sugars and Sugar Alcohols

[17] Of the various compounds identified, the sugars (trehalose, sucrose, glucose, fructose) and sugar alcohols (glycerol, erythritol, arabitol, mannitol and inositol) were found to be the most prevalent in the coarse fraction (Figure 1). Together they accounted for 62% of the coarse mass identified by GC-MS/IC during the day, and 78% during the night. All of these compounds have previously been identified in samples from the dry season [*Graham et al.*, 2002], where a general lack of correlation with various biomass-burning indicators was taken as evidence that they may have formed part of the natural background aerosol. The presence of the compounds in the current samples appears to confirm this hypothesis, with the higher coarse-fraction concentrations suggesting a likely association with the primary biogenic aerosol.

[18] There are many potential sources of sugars and sugar derivatives within the rainforest. A wide range of sugars and sugar alcohols are found in the fruits, flowers, guttation fluids, and tissues of plants [*Goatley and Lewis*, 1966; *Bartolozzi et al.*, 1997; *Adams et al.*, 1999]. Sugar alcohols and trehalose are well-known constituents of bacteria, fungi, lower plants and invertebrates [*Bieleski*, 1982], serving as reserve carbohydrates and/or cell protectants against stressful conditions [*Eleutherio et al.*, 1993; *Chaturvedi et al.*, 1997]. The extracellular matrices (ECM) of fungi, secreted films that aid in adhesion to plant surfaces, contain glycoproteins, which may degrade to yield saccharidic compounds [*Buck and Andrews*, 1999; *Doss*, 1999]. Insect fragments may have also contributed to the observed sugar/sugar alcohol levels, since insects themselves contain sugars, accumulate sugars while pollinating, and/or produce them while grazing on plants [*Chapman*, 1982].

[19] Figure 2 shows the average day and nighttime sugar/sugar alcohol concentrations for the fine and coarse aerosol fractions. Interestingly, airborne concentrations of trehalose, mannitol, and arabitol were found to be significantly higher at night, while glucose, fructose, and sucrose concentrations were consistently higher during the daytime. Moreover, good correlations were observed between pairs of sugars within each group, suggesting a common origin (Table 2). Similar associations between the sugars/sugar alcohols have been noted by other workers. *Pashynska et al.* [2002] found that for aerosol collected in Gent, Belgium, levels of glucose, sucrose, and fructose were highest in early summer (June), while arabitol and mannitol concentrations peaked together later in summer. They suggested that the sugars may have been associated with airborne detritus from developing leaves, and the sugar alcohols with detritus from mature leaves. *Maenhaut et al.* [2002] observed good correlations between glucose and fructose, as well as

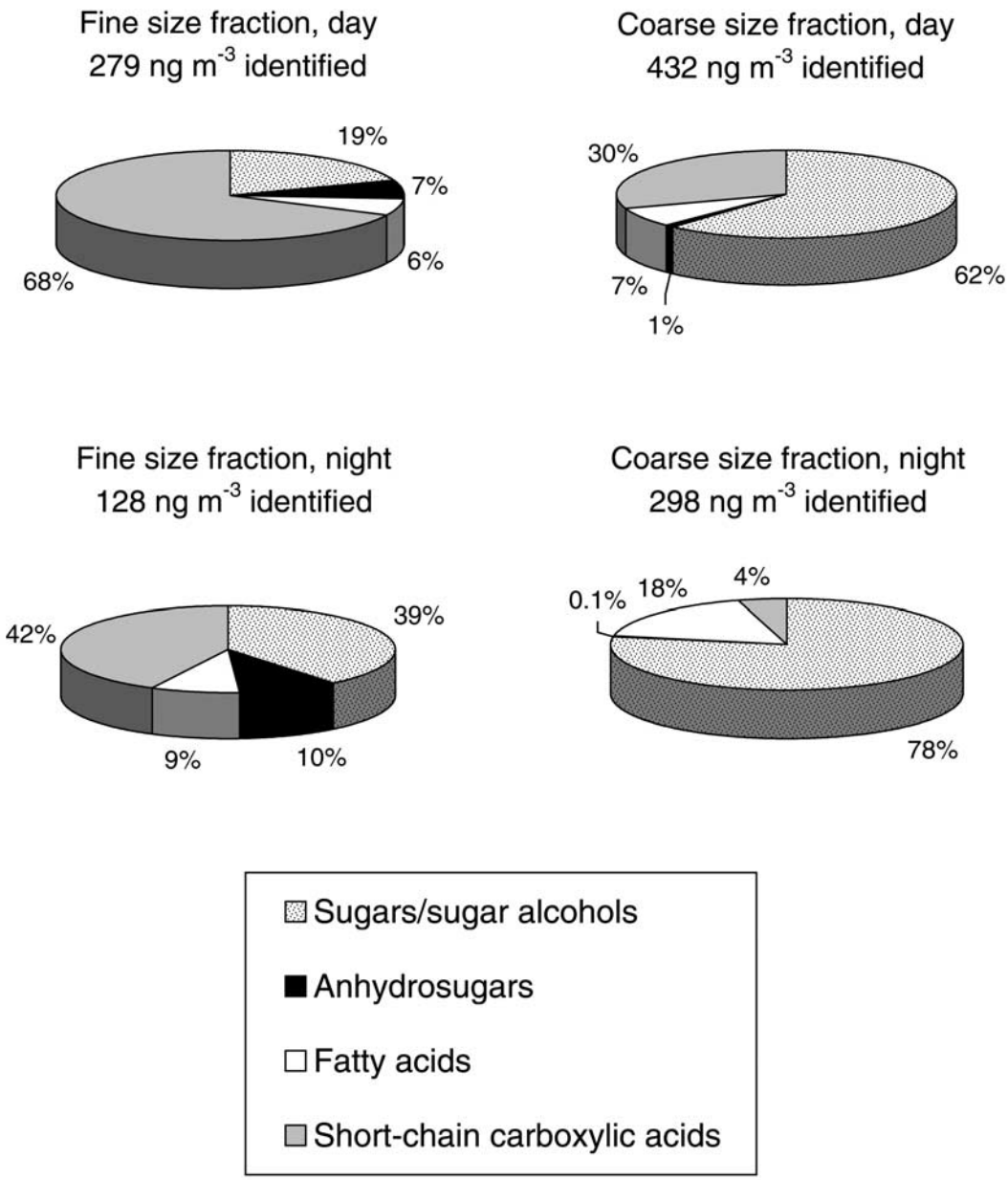

Figure 1. Mean contribution of sugars/sugar alcohols, anhydrosugars, fatty acids, and short-chain carboxylic acids to the composition of the organic matter identified by GC-MS and IC in day and nighttime atmospheric aerosol samples collected during the CLAIRE 2001 campaign (19–28 July 2001). The identified masses are the sum of the concentrations of the organic compounds quantified by GC-MS and IC.

between arabitol and mannitol, for aerosols collected during the SAFARI 2000 campaign in South Africa.

[20] On the basis of the similar observations recorded at such a diverse range of locations, it seems reasonable to conclude that there must exist two fairly generic sources for the two groups of sugars/sugar alcohols. Since arabitol, mannitol and trehalose are well-known constituents of fungal spores [*Lewis and Smith*, 1967; *Bieleski*, 1982], we hypothesize that the enhanced nighttime concentrations of these compounds may have been mainly associated with the observed nocturnal increase in yeasts and other small fungal spores [*Graham et al.*, 2003; P. E. Taylor et al., manuscript in preparation, 2003]. On the other hand, the higher glucose, fructose, and sucrose levels during the day coincide with the higher pollen, fern spore and insect (fragmented and whole) counts recorded for the day samples. While there is no sugar analysis available for fern spores in the literature, pollen grains are known to contain sucrose, glucose, and fructose [*Pacini*, 2000; *Willemse*, 2000; *Vesprini et al.*, 2002]. Many are richest in sucrose, but a few have higher glucose and fructose contents [*Pacini*, 2000]. Plant fragments are also a potential source for these sugars, although microscopic

Table 1. Mean, Median, Minimum, and Maximum Concentrations of Organic Carbon, Elemental Carbon, and Organic Compounds Detected in the Fine and Coarse Size Fractions of Atmospheric Aerosol Samples Collected During the CLAIRE 2001 Campaign (19–28 July 2001)[a]

	Fine Size Fraction					Coarse Size Fraction				
Species	Mean	Median	Minimum	Maximum	N^b	Mean	Median	Minimum	Maximum	N^b
OC	1130	1110	690	1550	6	2260	2250	1680	2720	6
EC	47	54	14	70	6	22	27	2	33	6
Sugars/Sugar Alcohols										
Glycerol	0.29	0.21	<0.06	0.41	4	2.06	1.66	1.14	4.00	6
Erythritol	0.54	0.51	0.40	0.87	6	1.84	1.79	1.13	2.46	6
Arabitol	13.84	10.87	7.08	25.65	6	41.74	31.49	16.07	93.44	6
Fructose	4.75	3.25	1.71	9.66	6	28.70	16.83	1.86	75.09	6
Glucose	7.86	6.95	1.88	16.32	6	47.95	33.65	1.65	124.49	6
Mannitol	15.17	14.75	9.58	24.38	6	53.30	50.79	23.69	101.79	6
Inositol	0.27	0.24	0.16	0.48	6	2.85	2.80	2.59	3.29	6
Sucrose	1.45	<0.54	<0.06	1.90	3	36.95	10.63	<0.06	77.10	4
Trehalose	6.88	6.04	4.89	11.77	6	48.07	37.86	21.16	89.71	6
Anhydrosugars										
Galactosan	0.19	<0.08	<0.04	0.37	3	0.12	<0.05	<0.04	0.12	2
Mannosan	0.28	0.16	0.08	0.84	6	0.08	<0.07	<0.05	0.10	2
Levoglucosan	14.99	11.27	7.73	32.91	6	1.97	1.07	<0.04	4.79	5
Fatty Acids										
Tetradecanoic acid	0.65	0.51	0.35	1.49	6	0.48	0.42	0.32	0.69	6
Pentadecanoic acid	0.49	0.38	0.31	1.09	6	0.38	0.36	0.31	0.51	6
Hexadecanoic acid	5.21	4.02	2.08	12.74	6	13.45	12.73	9.14	19.53	6
Heptadecanoic acid	0.41	0.36	0.21	0.70	6	0.25	0.23	0.19	0.36	6
Oleic acid	1.47	1.61	0.63	2.17	6	19.33	17.88	14.46	25.29	6
Octadecanoic acid	1.02	0.80	0.37	2.34	6	3.69	3.55	1.23	6.88	6
Nonadecanoic acid		<0.15	<0.12	<0.19	0		<0.14	<0.10	<0.17	0
Eicosanoic acid	0.29	0.26	0.18	0.44	6	0.53	0.52	0.32	0.82	6
Heneicosanoic acid		<0.13	<0.10	<0.16	0		<0.12	<0.09	<0.14	0
Docosanoic acid	0.90	0.94	0.57	1.21	6	1.03	1.09	0.58	1.33	6
Tricosanoic acid	0.44	0.35	<0.15	0.64	5	0.15	<0.18	<0.13	0.15	1
Tetracosanoic acid	1.37	1.36	0.91	1.81	6	1.89	1.62	<0.22	2.98	5
Pentacosanoic acid	0.32	<0.27	<0.16	0.41	3		<0.19	<0.14	<0.23	0
Hexacosanoic acid	0.93	0.96	0.51	1.24	6	0.26	<0.24	<0.15	0.28	2
Heptacosanoic acid		<0.22	<0.17	<0.28	0		<0.20	<0.15	<0.25	0
Octacosanoic acid	0.68	0.67	0.27	1.10	6	0.40	<0.21	<0.16	0.40	1
Short-Chain Acids										
Oxalic acid	56.99	44.14	8.79	148.09	6	62.77	43.65	<1.61	87.51	4
Malonic acid	21.55	17.34	4.40	47.88	6	19.00	11.08	<0.04	49.10	5
Maleic acid	0.37	0.37	0.19	0.55	6	0.19	0.17	<0.05	0.30	5
Succinic acid	4.94	4.00	2.11	8.02	6	2.71	2.10	0.76	7.48	6
Methylsuccinic acid	0.44	0.42	0.31	0.73	6	0.32	0.35	0.12	0.54	6
Fumaric acid	0.62	0.63	0.23	0.83	6	1.11	0.85	0.19	2.66	6
Glutaric acid	1.09	1.01	0.47	1.61	6	0.35	0.28	0.05	0.82	6
Adipic acid	0.61	0.55	0.30	0.97	6	0.22	<0.12	<0.06	0.26	3
cis-Pinic acid	0.61	0.27	<0.10	1.42	4	0.49	0.33	<0.09	0.99	5
Pimelic acid	0.20	<0.13	<0.10	0.20	1		<0.12	<0.09	<0.15	0
Suberic acid	0.48	0.49	0.31	0.66	6		<0.11	<0.08	<0.13	0
Phthalic acid	0.56	0.46	0.24	1.06	6	0.35	<0.26	<0.20	0.35	1
Ketopimelic acid	2.00	1.84	0.83	3.52	6	0.25	<0.11	<0.04	0.36	3
Tricarballylic acid	3.25	2.87	1.50	5.26	6	0.35	<0.15	<0.08	0.52	3
Azelaic acid	1.34	1.19	0.70	2.50	6	0.39	0.39	0.27	0.57	6
Glycolic acid	9.74	9.76	2.65	14.83	6	1.78	1.43	0.33	4.37	6
Glyceric acid	1.53	1.20	0.41	2.82	6	1.26	0.71	0.30	4.07	6
Malic acid	14.50	12.12	4.22	24.10	6	4.32	3.15	0.71	12.08	6
Tartaric acid	3.14	2.66	0.84	5.87	6	0.40	<0.05	<0.04	0.40	1
Total (% OC)[c]	**6.7**	**6.6**	**5.6**	**8.1**		**7.0**	**6.6**	**5.4**	**9.3**	

[a]Concentrations are in ng m^{-3}. Means were calculated using values above the quantitation limit (QL) only, while medians were calculated by setting values below the QL to the QL. In cases where more than half the values were below QL, reported median values are preceded by "<". OC, organic carbon; EC, elemental carbon.

[b]The number of samples in which the element was observed above its QL.

[c]Percentage of OC accounted for by the carbon component of the compounds quantified by GC-MS/IC.

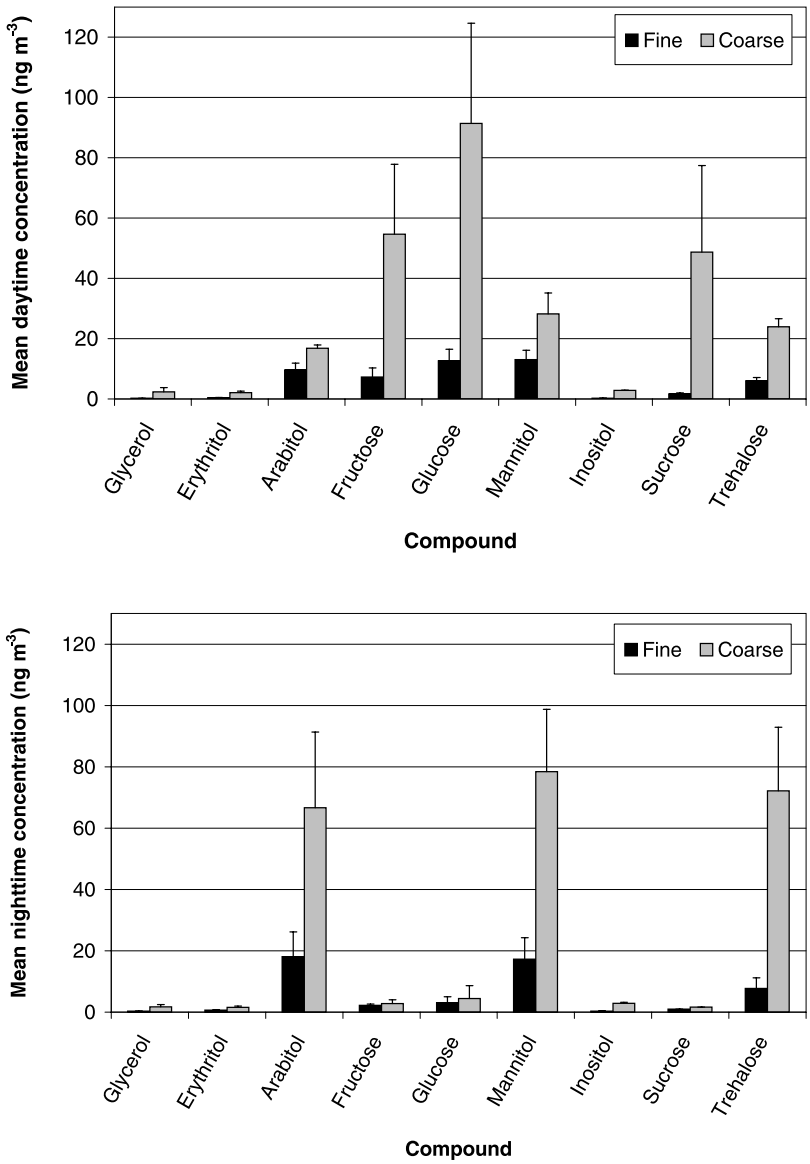

Figure 2. Mean (top) day and (bottom) nighttime sugar/sugar alcohol concentration profiles for atmospheric aerosol samples collected during the CLAIRE 2001 campaign (19–28 July 2001). The error bars represent one standard deviation.

analyses indicate that the contribution of leaf fragments to the total PBAP was very minor (P. E. Taylor et al., manuscript in preparation, 2003). The ratio of sugars in plants (nectar, fruit, leaves) is generally sucrose > fructose > glucose, although the nectars and fruits of some tropical and subtropical plants have glucose > sucrose > fructose [*Baker et al.*, 1998], and ancient plants (including ferns, mosses, and liverworts) appear to have a shift away from sucrose toward hexoses, such as glucose [*Baker et al.*, 1998]. Honeydew, produced by aphids, is a particularly rich source of glucose, fructose and sucrose [*Hendrix et al.*, 1992].

[21] Support for the proposed sources for the different sugars and sugar alcohols comes from the fact that the coarse-to-fine ratios for arabitol, mannitol, and trehalose were found to be significantly lower than for glucose, sucrose, and fructose. The more pronounced coarse-size distribution of the latter sugars during the day (Figure 2) is consistent with the fact that "giant" bioaerosol particles (pollen grains, fern spores, insects) would only be expected

Table 2. Pearson Correlation Table for the Major Sugars and Sugar Alcohols Identified in the Coarse Size Fraction of Atmospheric Aerosol Samples Collected During the CLAIRE 2001 Campaign (19–28 July 2001)

	Arabitol	Mannitol	Trehalose	Fructose	Glucose	Sucrose
Arabitol	1	0.967	0.979	−0.753	−0.763	−0.696
Mannitol	0.967	1	0.930	−0.779	−0.802	−0.734
Trehalose	0.979	0.930	1	−0.761	−0.780	−0.698
Fructose	−0.753	−0.779	−0.761	1	0.995	0.989
Glucose	−0.763	−0.802	−0.780	0.995	1	0.982
Sucrose	−0.696	−0.734	−0.698	0.989	0.982	1

to have collected on the coarse HiVol filter (the low levels in the fine fraction may be associated with cytoplasmic debris derived from the rupturing of pollen, as was sometimes observed by light microscopy (P. E. Taylor et al., manuscript in preparation, 2003)). Fungal spores, however, cover a wider size range (spores were also observed in the fine aerosol samples by electron microscopy (B. Graham et al., manuscript in preparation, 2003)), which might explain the significant levels of arabitol, mannitol, and trehalose that were observed in both size fractions of the aerosol (Figure 2). Fungal fragments may also contribute to the fine aerosol fraction [*Górny et al.*, 2002]. We note here that the hypothesized sources for the sugars/sugar alcohols also appear to be consistent with the observations of *Pashynska et al.* [2002] noted above, since pollen counts tend to be highest in late spring/early summer in temperate zones, while fungal spore concentrations peak in late summer or autumn, depending on rainfall.

[22] Overall, the fairly significant levels of the sugars and sugar alcohols observed in the samples lend additional support to the proposition of *Saxena and Hildemann* [1996] that poly-alcohols could constitute an important component of the water-soluble organic fraction of aerosols. Individual carbohydrate species have now been observed in aerosol samples from a variety of locations [*Wauters et al.*, 1979; *Nolte et al.*, 2001, 2002; *Suzuki et al.*, 2001; *Graham et al.*, 2002; *Pashynska et al.*, 2002], and NMR and FTIR studies have revealed a high OH-to-carbon ratio for several aerosol samples, which is seen as evidence for a substantial carbohydrate contribution [*Gundel et al.*, 1993; *Decesari et al.*, 2000; *Suzuki et al.*, 2001].

3.3.2. Anhydrosugars

[23] Relatively low levels of three anhydrosugars, levoglucosan, mannosan and galactosan, were found in the samples (Table 1), accounting for an average of only 8% of the fine aerosol mass identified by GC-MS/IC, and 0.5% of the coarse mass (Figure 1). These compounds are derivatives of glucose, mannose, and galactose, respectively, and are formed through the pyrolysis of cellulose and hemicelluloses present in biomass [*Shafizadeh*, 1984]. They have previously been identified as a major component of organic particulate matter in areas impacted by wood smoke [*Simoneit et al.*, 1999; *Graham et al.*, 2002; *Zdráhal et al.*, 2002] and are excellent source-specific tracers for biomass burning.

[24] As expected, the anhydrosugars were confined largely to the fine fraction (Table 1), since smoke aerosol consists predominantly of submicron accumulation mode particles [*Kleeman et al.*, 1999]. No consistent day-night variation in their concentrations was observed. Burning in Balbina and neighboring regions was probably the major source of the compounds, although long-range transported smoke aerosol may have also contributed. The average fine-fraction concentration of levoglucosan (the major anhydrosugar) was found to be 15 ng m^{-3}, as compared to average levels of 1200 and 2500 ng m^{-3} measured at forest and pasture sites, respectively, during the burning season in Rôndonia state (southwestern Amazon) in 1999 [*Graham et al.*, 2002]. On the basis of the average levoglucosan-to-OC ratio measured for the fine dry season aerosol [*Graham et al.*, 2002], and assuming comparable size distributions for smoke particles in the regional haze of Rôndonia and in the aged aerosol at Balbina, we estimate that smoke particles were responsible for 7–26% of the OC content of the fine aerosol fraction during the CLAIRE 2001 campaign. Thus the major fraction of OC measured in both the fine and coarse aerosol fractions during the present study [*Graham et al.*, 2003] appears to have been predominantly associated with biogenic emissions. Given that ~70% and 80% of the fine and coarse aerosol fractions, respectively, were found to be comprised of organic matter [*Graham et al.*, 2003], it therefore seems reasonable to conclude that biogenic aerosol particles constitute the bulk of the aerosol mass present over the Amazon Basin under nonpolluted background conditions.

3.3.3. Fatty Acids

[25] A series of long-chain *n*-fatty acids ($C_{13} - C_{24}$) were measured in the samples (Table 1), with hexadecanoic acid (C_{16}) and oleic acid ($C_{18:1}$) being the dominant species, as often observed for samples collected in remote locations [*Simoneit*, 1989]. While fatty acids may derive from a variety of sources, the strong even-to-odd carbon preference is indicative of biogenic input from lipid residues from microflora (bacteria, algae, fungi, etc.) and epicuticular waxes of vascular plants [*Simoneit*, 1989; *Rogge et al.*, 1993a, 1993b]. *Simoneit and Mazurek* [1981] and *Simoneit* [1989] have noted that fatty acids $<C_{20}$ are derived primarily from microbial sources, while the minor homologues $>C_{20}$ are associated largely with plant wax [*Simoneit and Mazurek*, 1981; *Simoneit*, 1989]. As noted earlier, the contribution of leaf fragments to the total PBAP in the CLAIRE 2001 samples was found to be relatively minor (P. E. Taylor et al., manuscript in preparation, 2003), suggesting that other biogenic components in the samples (whole and ruptured pollen, fern and fungal spores) were probably responsible for the bulk of the fatty acids measured in the sampled aerosol.

[26] As first noted by *Kubátová et al.* [2000] for samples collected during the CLAIRE 98 campaign, the fatty acids were generally more concentrated in the coarse aerosol fraction (average total of 41 ng m^{-3}) than the fine one (average total of 14 ng m^{-3}). In the coarse fraction, the average total concentration of fatty acids was somewhat higher for the nighttime samples (50 ng m^{-3}) compared to the daytime ones (32 ng m^{-3}), while for the fine fraction, the reverse was true (11 ng m^{-3} versus 17 ng m^{-3}). The higher nighttime concentrations observed for the coarse size fraction suggest that it is likely that fungal spores, more prevalent at night, were a major source for the fatty acids, especially given that there is unlikely to have been much plant wax released via abrasion of leaves during the still nights, and that the ECM of fungi are known to contain a range of fatty acids and other lipid classes [*Doss*, 1999; *Cooper et al.*, 2000]. The less pronounced diurnal variability compared to that found for the sugars/sugar alcohols, however, is consistent with the multiple biogenic origins of the fatty acids. Pollen grains, for example, also contain a range of lipids [*Wang et al.*, 2002], and would have contributed to the daytime concentrations of the fatty acids.

[27] In addition to the fatty acids, we also observed some long-chain *n*-alkan-1-ols in the samples (mostly with even carbon numbers from C_{26} to C_{32}), which have been reported as good indicators for vegetative detritus emissions [*Rogge et al.*, 1993a; *Nolte et al.*, 2002], although they may also

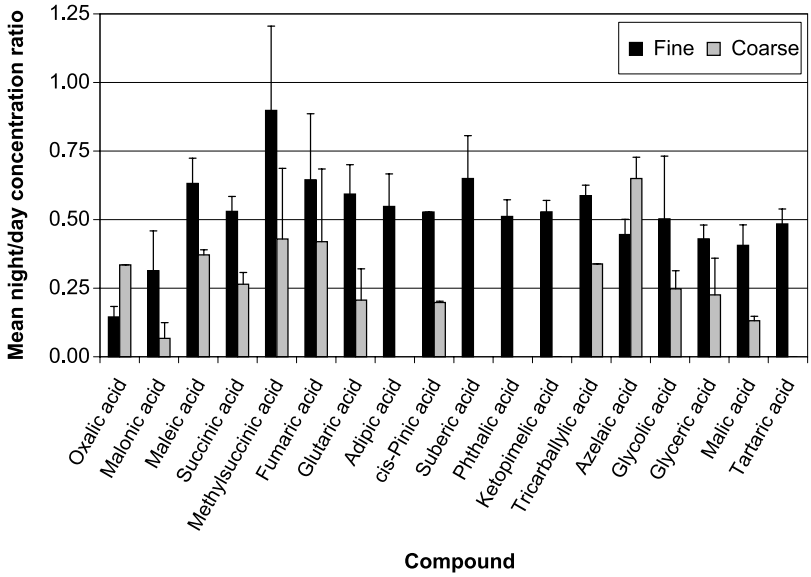

Figure 3. Mean ratios of nighttime-to-daytime concentrations of short-chain carboxylic acids for the fine and coarse atmospheric aerosol samples collected during the CLAIRE 2001 campaign (19–28 July 2001). The error bars represent one standard deviation.

potentially derive from the hydrolysis of wax esters present in the ECM of fungi [*Cooper et al.*, 2000]. Although we did not quantify these, the most prolific was octacosanol (C_{28}), which has previously been found to be one of the most dominant fatty alcohols present in rural and remote aerosols [*Simoneit and Mazurek*, 1981].

3.3.4. Short-Chain Carboxylic Acids

[28] The final group of compounds that were quantified in the samples were a series of dicarboxylic, tricarboxylic, keto and hydroxyacids. It should be noted that the extraction efficiencies of organic acids into methanol may only be high when they are present in their neutral (acid) form. It is likely that a sizeable fraction of the acids were actually present in the samples in their less-soluble salt forms, and therefore it should be cautioned that the values presented in Table 1 may underestimate the actual atmospheric concentrations (acidification of the samples to improve the extraction efficiency of the acids was not attempted in this study because of the risk of forming methyl esters, as well as of hydrolyzing the disaccharides, sucrose and trehalose). Nonetheless, we present our concentration data set for these compounds because a number of interesting trends were observed, particularly with regard to diurnal variability.

[29] Short-chain dicarboxylic and tricarboxylic acids have been identified as ubiquitous organic aerosol constituents, which may derive from primary emissions or from secondary photochemical reactions in the atmosphere [*Grosjean et al.*, 1978; *Kawamura and Ikushima*, 1993; *Stephanou and Stratigakis*, 1993; *Kawamura et al.*, 1996; *Limbeck and Puxbaum*, 1999; *Neusüss et al.*, 2000; *Kubátová et al.*, 2002]. All of the acids we identified have been observed previously. Together, they accounted for an average of 55 and 17% of the fine and coarse aerosol mass identified by GC-MS/IC, respectively, with the percentage proportions higher for the daytime samples (Figure 1). The concentrations were generally lower than those found during the dry season [*Graham et al.*, 2002], but are fairly comparable to those reported by *Limbeck et al.* [2001] for a subtropical savanna background site in South Africa. Oxalic acid was found to be the dominant diacidic species, followed by malonic, malic, and succinic acids (Table 1). The predominance of these acids has previously been observed at a range of locations throughout the world [*Kawamura and Ikushima*, 1993; *Limbeck and Puxbaum*, 1999]. The presence of oxalic acid in aerosol collected at a remote forest site was first reported by *Norton et al.* [1983], who ascribed it to long-range transported anthropogenic pollution.

[30] Figure 3 shows the average nighttime-to-daytime concentration ratios measured for the short-chain acids (note: ratios could not be determined for some acids because of too few data above the quantitation limit). These compounds exhibited a distinctly different temporal behavior to the other organic compounds identified by GC-MS, with generally higher concentrations in the daytime samples (ratios below unity). Together with their predominantly fine-fraction distribution (Table 1), this indicates that the acids may have been largely associated with biogenic SOA, derived from the photooxidation of VOCs emitted from the forest [*Went*, 1960; *Andreae and Crutzen*, 1997; *Kavouras et al.*, 1999a, 1999b]. Enhanced daytime concentrations of dicarboxylic acids have been reported previously by a number of workers [*Schuetzle et al.*, 1975; *Satsumabayashi et al.*, 1990; *Kavouras et al.*, 1999b; *Souza et al.*, 1999], and are generally seen as evidence for a photochemical source. In the present case, it should be noted that the higher daytime concentrations (measured at ground level) may also reflect the effect of enhanced downward mixing of organic acid-bearing aerosol from aloft. Such aerosol may have included a long-range transported component, but perhaps more significantly, SOA formed at higher altitudes, where OH radical levels are highest and the possibility exists for liquid-phase production of organic acids within cloud droplets [*Jacob*, 1986; *Blando and Turpin*, 2000; *Warneck*, 2003].

[31] Amongst the various dicarboxylic acids that we identified in the samples, one that is worthy of special mention is *cis*-pinic acid, a well-known photooxidation product of monoterpenes such as α-pinene and β-pinene [*Calogirou et al.*, 1999]. The measured concentrations of this compound were consistently very low (Table 1). The mean value is comparable to the aerosol-phase values reported by *Yu et al.* [1999] for two national park sites in America (0.5 ng m^{-3}), but is substantially lower than those reported by *Kavouras et al.* [1999a] for a Eucalyptus forest in Portugal (0.4–82.7 ng m^{-3}), and by *Kavouras et al.* [1999b] for a conifer forest in Greece (0.4–4.4 ng m^{-3}). Moreover, in contrast to *Kavouras et al.* [1999a, 1999b] and *Yu et al.* [1999], we did not detect any pinonic acid in our samples, although this is another major monoterpene oxidation product [*Calogirou et al.*, 1999]. As noted by *Yu et al.* [1999], the large variability of the aerosol-phase concentrations between sites may reflect the fact that the gas-aerosol partitioning of *cis*-pinic and pinonic acids is sensitive to both temperature and the overall aerosol chemical composition. In addition, both positive sampling artifacts (adsorption of gas-phase semivolatiles) and negative sampling artifacts (volatilization) may heavily influence the measured concentrations. Nonetheless, the present data appear to indicate that the contribution of *cis*-pinic and pinonic acids to the aerosol over the Amazon rainforest is fairly minimal. It may be that other oxidative degradation products are preferentially formed from monoterpenes and other VOCs emitted by the forest, such as the dicarboxylic and tricarboxylic acids and ketoacids recently identified by *Kubátová et al.* [2000] and *Zdráhal et al.* [2001]. M. Claeys et al. (Formation of secondary organic aerosols through photooxidation of isoprene, submitted to *Science*, 2003) have recently presented evidence that methyltetrols formed from the photooxidation of isoprene also appear to make a significant contribution to SOA over the Amazon Basin.

[32] Interestingly, fairly significant amounts of some of the acids were found in the coarse size fraction of the aerosol samples (Table 1). This may have been due to condensation of photooxidation products onto large preexisting aerosol particles, or fine-to-coarse redistribution of the acids due to their semivolatile nature [*Limbeck et al.*, 2001]. Some of the acids in the coarse fraction may have also been associated with vegetation detritus, since a wide range of acids are known to be present in the guttation fluids, fruits and tissues of plants [*Goatley and Lewis*, 1966; *Bartolozzi et al.*, 1997; *Adams et al.*, 1999]. We note, however, that *Rogge et al.* [1993a] did not observe dicarboxylic acids in their analyses of particulate abrasion products from the leaf surfaces of plants. Other sources for the coarse fraction diacids could have included the nonleaf fragment PBAP particles observed in the samples, i.e., pollen grains, fern and fungal spores. Ozonolysis of sporopollenin, the material making up the outermost protective wall of pollen, algae, fungi, moss, and fern spores, is known to produce short-chain dicarboxylic acids as major degradation products [*Domínguez et al.*, 1999].

[33] Overall, the carbon content of the organic species quantified by GC-MS accounted for an average of 7% of the OC in both the fine and coarse aerosol fractions [*Graham et al.*, 2003]. Individual organic compounds insoluble in methanol and/or not amenable to GC-MS analysis because of their low volatility (including naturally occurring humic and fulvic acids [*Havers et al.*, 1998]) may have constituted a significant fraction of the unidentified material. However, the vast majority of the remaining OC was likely in the form of complete or fragmented primary biological structures, such as spores, pollen, algae, bacteria, leaf and insect parts. Indeed, based on an estimate of the OC content of fungal spores (13 pg C $spore^{-1}$) [*Bauer et al.*, 2002a, 2002b], our microscopic observations [*Graham et al.*, 2003; P. E. Taylor et al., manuscript in preparation, 2003] suggest that fungal spores alone could have been responsible for approximately 0.3 and 3 μg OC m^{-3} during the day and nighttime, respectively. Because such a major fraction of the OC is "locked up" in cellular structures, either as biopolymers like proteins, cellulose and other polysaccharides [*Puxbaum and Tenze-Kunit*, 2003], or as low-molecular-weight compounds inside intact cells, techniques such as GC-MS can never be expected to explain more than a small fraction of the organic aerosol mass (at least for tropical forested areas). This is an important point to stress, especially given the emphasis of much of the scientific literature concerning organic aerosol characterization on attempting to speciate the OC fraction in terms of single compounds.

[34] Many of the compounds identified by the GC-MS method are highly polar, multifunctional compounds that are water soluble. Aside from the fatty acids, all fall into the major compound classes that *Saxena and Hildemann* [1996] speculated would contribute to the water-soluble fraction of aerosols, and support the notion that bioaerosols are a source of water-soluble compounds, rather than just insoluble waxes. While intact biological particles themselves may not be expected to be efficient CCN, due to their outer protective hydrophobic membrane, such water-soluble compounds may potentially contribute to the ability of particles to act as CCN and also participate in the complex organic liquid-phase chemistry of clouds [*Facchini et al.*, 1999; *Jacobson et al.*, 2000; *Nenes et al.*, 2002; *Roberts et al.*, 2002]; however, further studies are required to establish whether this is indeed the case.

4. Summary and Concluding Comments

[35] In this study, the diurnal variations of several organic compounds present in the natural Amazonian aerosol were examined by analyzing a series of day-night segregated samples collected during the CLAIRE 2001 campaign. For a number of the compounds, the predominant coarse mode distribution and diurnal patterns we observed provide compelling evidence for an association with PBAP emitted from the forest. In particular, trehalose, arabitol and mannitol appear to be associated with yeasts and other fungal spores present in higher concentrations at night, while glucose, fructose and sucrose are linked with the specific daytime release of pollen, fern spores and other "giant" bioaerosols. These compounds represent useful additions to the list of compounds that are used as tracers for different types of PBAP, a list that currently includes the homologous lipid series, terpenes, phytosterols [*Simoneit*, 1989], 3-hydroxy fatty acids, muramic acid [*Krahmer et al.*, 1998], and phospholipids [*MacNaughton et al.*, 1999; *Womiloju et al.*, 2003]. We have already shown that a number of the

sugars/sugar alcohols do not appear to be correlated with biomass burning [*Graham et al.*, 2002]. Therefore they may ultimately prove to be useful in helping to determine the relative contributions of natural and anthropogenic components to the total aerosol loading over areas influenced by biomass burning, which is critical for assessing the impact of large-scale biomass burning emissions on atmospheric chemistry and climate.

[36] For the fine aerosol size fraction, higher concentrations of a range of oxygenated organic acids were measured in samples collected during the daytime, which provides some indication for a contribution of SOA to the background aerosol. While we are unable to quantify the magnitude of this contribution, the low concentrations of levoglucosan and other anhydrosugars measured in the samples suggest that biomass burning aerosol was responsible for only a small amount of the OC content of the fine aerosol. Thus it is likely that the major mass fraction of the fine aerosol, estimated to be composed of ~70% organic matter [*Graham et al.*, 2003], was constituted of biogenic particles, many of which can be expected to have been of secondary origin, although small fungal spores and other PBAP also made a substantial contribution (B. Graham et al., manuscript in preparation, 2003). Given the known cloud droplet and ice nucleating properties of biogenic aerosol particles [*Schnell and Vali*, 1973, 1976; *Franc and DeMott*, 1998; *Diehl et al.*, 2001; *Bauer et al.*, 2003], it is therefore possible that the large-scale deforestation occurring within the Amazon forest has the potential to impact dramatically on the biogenically regulated CCN population, and therefore the radiation budget and precipitation patterns in the region. The observation of a dominant biogenic contribution to the fine aerosol fraction appears particularly significant because these small particles could potentially be transported to the free troposphere by tropical convection. The effects of land use changes may, therefore, be propagated to higher-latitude regions because of the deep convective activity associated with the ITCZ and Hadley circulations in the tropics [*Garstang et al.*, 1988; *Andreae et al.*, 2001].

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